Phase control of La_2CuO_4 in thin-film synthesis

A. Tsukada*
Department of Physics, Science University of Tokyo,
1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

T. Greibe†
NTT Basic Research Laboratories, NTT Corporation,
3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

M. Naito
NTT Basic Research Laboratories, NTT Corporation,
3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan and
Department of Physics, Science University of Tokyo,
1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
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The lanthanum copper oxide, La_2CuO_4, which is an end member of the prototype high-T_c superconductors $(La,Sr)_2CuO_4$ and $(La,Ba)_2CuO_4$, crystallizes in the "K_2NiF_4" structure in high-temperature bulk synthesis. The crystal chemistry, however, predicts that La_2CuO_4 is at the borderline of the K_2NiF_4 stability and that it can crystallize in the Nd_2CuO_4 structure at low synthesis temperatures. In this article we demonstrate that low-temperature thin-film synthesis actually crystallizes La_2CuO_4 in the Nd_2CuO_4 structure. We also show that the phase control of "K_2NiF_4"-type La_2CuO_4 versus "Nd_2CuO_4"-type La_2CuO_4 can be achieved by varying the synthesis temperature and using different substrates.

I. INTRODUCTION

The rare earth copper oxides of the general chemical formula RE_2CuO_4 take two different crystal structures: K_2NiF_4 (abbreviated as " T ") and Nd_2CuO_4 (" T' "). The structural difference between T and T' can be viewed simply as the difference in the RE-O arrangements: rock-salt-like versus fluorite-like. With regard to the Cu-O coordination, however, there is a significant difference: T has octahedral CuO_6, whereas T' has two-dimensional square-planar CuO_4. Empirically, the former accepts only hole doping, the latter only electron doping. The T structure is formed with large La^{3+} ions, while the T' structure is formed with smaller RE^{3+} ions, such as RE = Pr, Nd, Sm, Eu, and Gd[1]. The T-T' boundary lies between La^{3+} and Pr^{3+}. Namely, La_2CuO_4 is at the borderline of the T-phase stability.

The crystal chemistry of the rare earth copper oxides has been explained in terms of the crystallographic tolerance factor (t)[2,3], which is defined as

$$t = \frac{r_i(\mathrm{RE}^{3+}) + r_i(\mathrm{O}^{2-})}{\sqrt{2} \times \{r_i(\mathrm{Cu}^{2+}) + r_i(\mathrm{O}^{2-})\}} \tag{1}$$

where $r_i(\mathrm{RE}^{3+})$, $r_i(\mathrm{Cu}^{2+})$, and $r_i(\mathrm{O}^{2-})$ are the ionic radii for RE^{3+}, Cu^{2+}, and O^{2-} ions. The t values for La_2CuO_4 and Pr_2CuO_4 are evaluated as 0.8685 and 0.8562 using the room-temperature ionic radii by Shannon and Prewitt[4]. From the extensive data collected for a variety of RE_2CuO_4-type cuprates, the critical (room-temperature) value for the T $\rightarrow$ T' transition is presumed to be $t_c = 0.865$, below which T is unstable[2,3].

The different thermal expansion ("thermal-expansion mismatch") between the RE-O and Cu-O bond lengths plays an important role in the T-versus-T' stability as pointed out initially by Manthiram and Goodenough[5]. The "ionic" RE-O bond has a larger thermal expansion than the "covalent" Cu-O bond, which leads to the increase in t with increasing temperature. Hence the T phase is stable at high temperatures whereas the T' phase is stable at low temperatures. In the case of La_2CuO_4, the transition from T to T' is predicted to occur at around 700 K (427°C), where $t(700\ \mathrm{K}) \sim 0.88$. There have been a few attempts to stabilize the T' phase of La_2CuO_4 in the past. However, a conventional solid-state reaction method requires firing temperature of at least 500°C even with coprecpitated fine powders, so it could not produce single-phase T'-La_2CuO_4. Bulk synthesis of T'-La_2CuO_4 has been achieved only by a very special recipe as given by Chou *et al.*[6] Their recipe consists of the following two steps. The first step is to reduce T-La_2CuO_4 with hydrogen around 300°C and obtain the Sr_2CuO_3-like phase. The second step is to convert the Sr_2CuO_3-like phase to T'-La_2CuO_4 by reoxygenation below 400°C. The resultant product was the single-phase T', although x-ray peaks were broadened due to the considerable lattice disorder and defects.

In thin-film synthesis, the reaction temperature can be lowered significantly, since reactants are much smaller in size and also more reactive than in bulk synthesis. The reactants in thin-film synthesis are atoms or molecules

or ions or clusters, depending on the technique employed. The limiting case is achieved by reactive coevaporation from metal sources, in which the reactants are atoms and the oxidation reaction is initiated on a substrate. Using this reactive coevaporation technique, we have learned from our ten-year experience that cuprate films crystallize at temperatures as low as 400°C. This enabled us to synthesize single-phase T'-La_2CuO_4. In this article we describe the phase control of "K_2NiF_4"-type La_2CuO_4 versus "Nd_2CuO_4"-type La_2CuO_4 by varying the synthesis temperature and using different substrates.

II. EXPERIMENT

We grew La_2CuO_4 thin films in a customer-designed MBE chamber from metal sources using multiple electron-gun evaporators with accurate stoichiometry control of the atomic beam fluxes. During growth, RF activated atomic oxygen was used for oxidation. The chamber pressure during growth was 6×10^{-6} Torr. The substrate temperature was varied from 425°C to 725°C. The growth rate was ~ 1.5 Å/s, and the film thickness was typically 450 Å. After the evaporation, most of the films were cooled to temperatures lower than 200°C at a rate lower than 20°C/min in 1×10^{-5} Torr molecular oxygen to avoid phase decomposition. Some of the films were cooled in vacuum or in ozone to investigate the change of the transport properties by excess oxygen.

In order to examine the substrate influence on the selective phase stabilization[7], we used various substrates as listed in Table 1. The in-plane lattice constant (a_s) covers from 3.6 Å to 4.2 Å , which should be compared to $a_0 = 3.803$ Å for T-La_2CuO_4 and $a_0 = 4.000$ - 4.010 Å for T'-La_2CuO_4 (T-La_2CuO_4 has orthorhombic structure with $a' = 5.3574$ Å and $b' = 5.4005$ Å, and a_0 is calculated as $\sqrt{(a' \times b')/2}$). The crystal structures include perovskite, K_2NiF_4, NaCl, and CaF_2 (fluorite). We deposited films simultaneously on all the substrates listed in Table 1, which were pasted to one substrate holder by Ag paint. This avoids run-to-run variations.

The lattice parameters and crystal structures of the films were determined using a standard x-ray diffractometer. Resistivity was measured by the standard four-probe method using electrodes formed by Ag evaporation.

III. RESULTS AND DISCUSSION

A. Effect of synthesis temperature on the selective phase stabilization

Figure 1 shows the x-ray diffraction (XRD) patterns of La_2CuO_4 films grown on $NdCaAlO_4$ (NCAO) substrates with different synthesis temperatures (T_s). Since the c-axis lattice constant (c_0) is distinct between T and T' (c_0(T) = 13.15 Å versus c_0(T') = 12.55 Å), the phase identification is rather straightforward. The calculated patterns for T and T' are also included in Fig. 1. The films grown at $T_s > 625$°C are single-phase T, while the films grown at T_s = 500 - 550°C are single-phase T'. The films grown at T_s = 575 - 600°C are a two-phase mixture of T and T' with T' more dominant for lower T_s. The films grown below T_s = 475°C show unidentified peaks at $2\theta \sim 31.4°$ and 65.5°. From this result, we can see the following trend for synthesis temperature on the selective phase stabilization. High T_s stabilizes T and low T_s stabilizes T'.

B. Effect of substrates on the selective phase stabilization

Figure 2 shows the XRD patterns of La_2CuO_4 films grown at T_s = 525°C on different substrates. Of these films in this figure, the films on $KTaO_3$ (KTO), NCAO, and ZrO_2(Y) (YSZ) are single-phase T'[8], while the films on $LaSrGaO_4$ (LSGO), $LaAlO_3$ (LAO), $LaSrAlO_4$ (LSAO), $PrSrAlO_4$ (PSAO), and $NdSrAlO_4$ (NSAO) are single-phase T. On $YAlO_3$, the film is dominantly T' with a trace amount of T. On $SrTiO_3$ (STO) and $NdGaO_3$ (NGO), the films are clearly a mixture of T and T'. The film on STO contains some amount of the T*-like (!) phase[9]. On MgO (MGO), no clear peak is observed. The c_0 values of these films together with films on other substrates are summarized in Fig. 3. Because of epitaxial strain[10], c_0 of the T structure is noticeably substrate-dependent: the longest (c_0 = 13.25 Å) for LSAO and the shortest (c_0 = 13.05 Å) for LSGO. From these results, we can see the following trend for a substrate lattice parameter on the selective phase stabilization. Substrates with a_0 of 3.70 - 3.85 Å stabilize T, and substrates with a_0 of > 3.90 Å or < 3.70 Å stabilize T' (or destabilize T).

Next we mention the effect of substrate crystal structure on the selective phase stabilization. If, in Fig. 2, one compares the films grown on perovskite and K_2NiF_4-type substrates with almost the same a_0, for example, NGO (a_0 = 3.838 Å) vs LSGO (a_0 = 3.843 Å) or YAO (a_0 = 3.715 Å) vs NSAO (a_0 = 3.712 Å), one can notice the trend that K_2NiF_4-type substrates have a tendency to stabilize the T structure rather than the T' structure.

C. Phase diagram in the T_s-a_s plane

Our survey was performed at T_s from 425°C to 725°C on all substrates in Table 1. Figure 4 summarizes the results, which show the phase diagram on the selective stabilization of T versus T' in the T_s-a_s plane.
High T_s *(625 ∼ 725° C)*
The films on most of the substrates are single-phase T. There are three exceptional substrates: KTO, YAO, and YSZ. The films on KTO and YSZ do not show any definite x-ray peak. The film on YAO is a mixture of T and T' even at the highest temperature investigated. This can be explained by interdiffusion of Y from YAO substrates into La_2CuO_4 since Y substitution for La is known to stabilize the T' structure.
Low T_s *(450 ∼ 600° C)*
The films on the T-lattice matched substrates (LSGO, LAO, LSAO, PSAO, and NSAO) are single-phase T. The films on T'-lattice matched KTO and on fluorite YSZ are single-phase T'. The films on other substrates (STO, NGO, YAO, and NCAO) are a two-phase mixture of T and T' with T' more dominant for lower T_s.

D. Comparison of T-La_2CuO_4 and T'-La_2CuO_4

Next, we make a brief comparison of the physical properties of T-La_2CuO_4 and T'-La_2CuO_4, which have the same chemical formula but different crystal structures. Figure 5 shows the temperature dependences of resistivity for both the phases. The solid lines represent the ρ - T curves for the films cooled in vacuum to ambient temperature, which do not have excess oxygen but might have slight oxygen deficiencies ($La_2CuO_{4+\delta}$ with $\delta \sim 0$). The broken lines represent those for the films cooled in ozone, which have interstitial excess oxygen ($\delta > 0$)[11]. The excess oxygen occupies the tetrahedral site in T, and the apical site in T'. The vacuum-cooled T film has much higher resistivity (by several orders of magnitudes at low temperatures) than the vacuum-cooled T' film. In fact, T'-La_2CuO_4 is metallic down to 180 K[12]. The ozone cooling causes a totally opposite effect on T and T'. The resistivity of the T film gets lowered by five orders of magnitudes at room temperature from $\sim 50\ \Omega \cdot$cm to $\sim 5 \times 10^{-4}\ \Omega \cdot$cm, indicating that holes doped by excess oxygen are itinerant. Furthermore the film becomes superconducting. In contrast, the resistivity of the T' film increases, indicating that holes doped by excess oxygen are localized[12].

IV. SUMMARY

In summary, we have demonstrated that La_2CuO_4 can crystallize in the Nd_2CuO_4 structure using low-temperature thin-film synthesis. Furthermore the phase control of "K_2NiF_4"-type La_2CuO_4 versus "Nd_2CuO_4"-type La_2CuO_4 can be achieved by varying the synthesis temperature and also the substrate. The general trends are as follows: (i) high T_s stabilizes T and low T_s stabilizes T', (ii) substrates with $a_s \sim 3.70$ - 3.85 Å stabilize T and substrates with $a_s >$ 3.90 Å or $a_s <$ 3.70 Å stabilize T' (or destabilize T), and (iii) K_2NiF_4-type substrates stabilize T.

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* Electronic address: tsukada@with.brl.ntt.co.jp
† On leave from Technical University of Denmark.
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TABLE I: Crystal structure and a-axis lattice constant (a_s) for the substrates used in this work. The in-plane lattice constants (a_0) for T'-La_2CuO_4 and T-La_2CuO_4 are also included.

Substrate	Abbreviation	a_s or a_0 (Å)	Crystal structure
MgO (100)	MGO	4.212	NaCl
$KTaO_3$ (100)	KTO	3.989	perovskite
$SrTiO_3$ (100)	STO	3.905	perovskite
$LaSrGaO_4$ (001)	LSGO	3.843	K_2NiF_4
$NdGaO_3$ (100)	NGO	3.838	perovskite
$LaAlO_3$ (100)	LAO	3.793	perovskite
$LaSrAlO_4$ (001)	LSAO	3.755	K_2NiF_4
$PrSrAlO_4$ (001)	PSAO	3.727	K_2NiF_4
$YAlO_3$ (100)	YAO	3.715	perovskite
$NdSrAlO_4$ (001)	NSAO	3.712	K_2NiF_4
$NdCaAlO_4$ (001)	NCAO	3.688	K_2NiF_4
ZrO_2 (Y) (100)	YSZ	3.616	fluorite
T'-La_2CuO_4		4.005	Nd_2CuO_4
T-La_2CuO_4		3.803	K_2NiF_4

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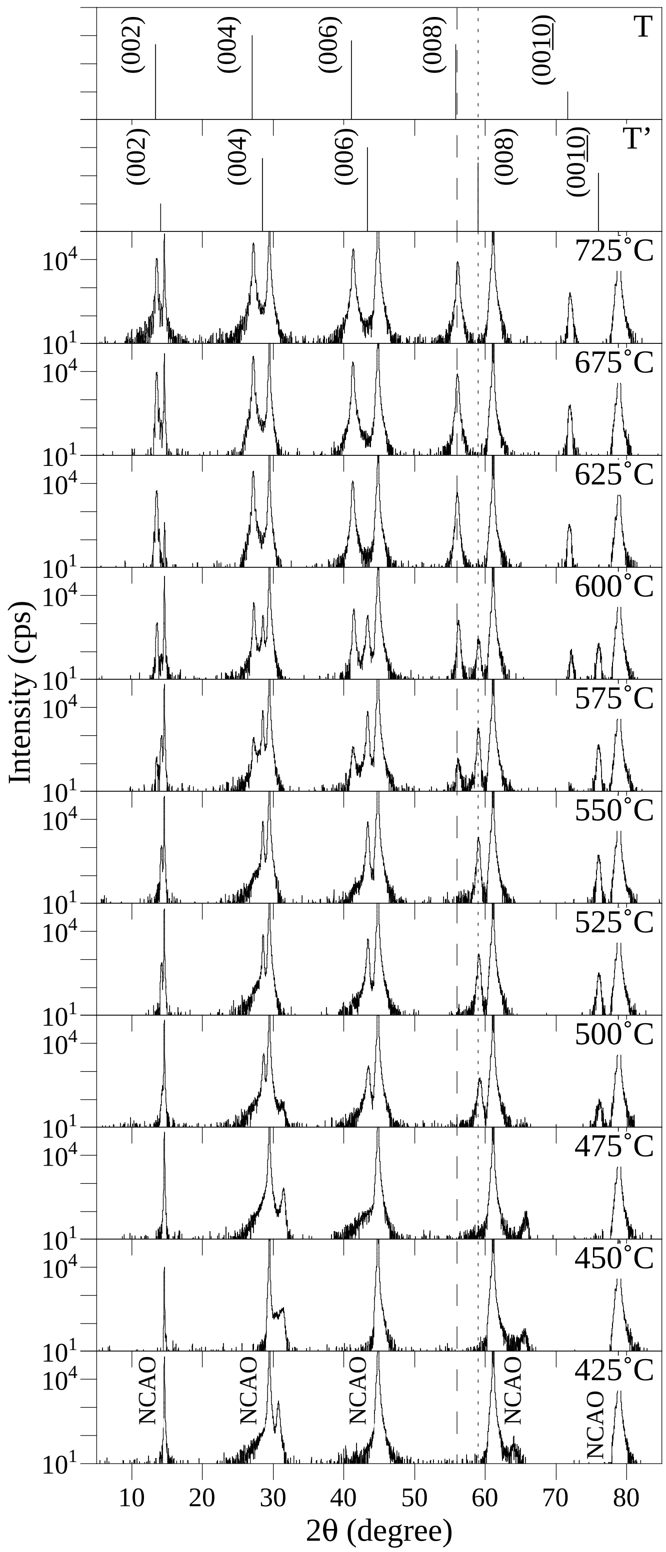

FIG. 1: XRD patterns for La_2CuO_4 films grown on NCAO substrates at T_s = 725 - 425°C. The top two patterns are simulations for the T and T' structure. The broken and dotted lines indicate the peak positions of the (008) line for the T and T' structure, respectively. Peak positions of NCAO are indicated in the lowest figure.

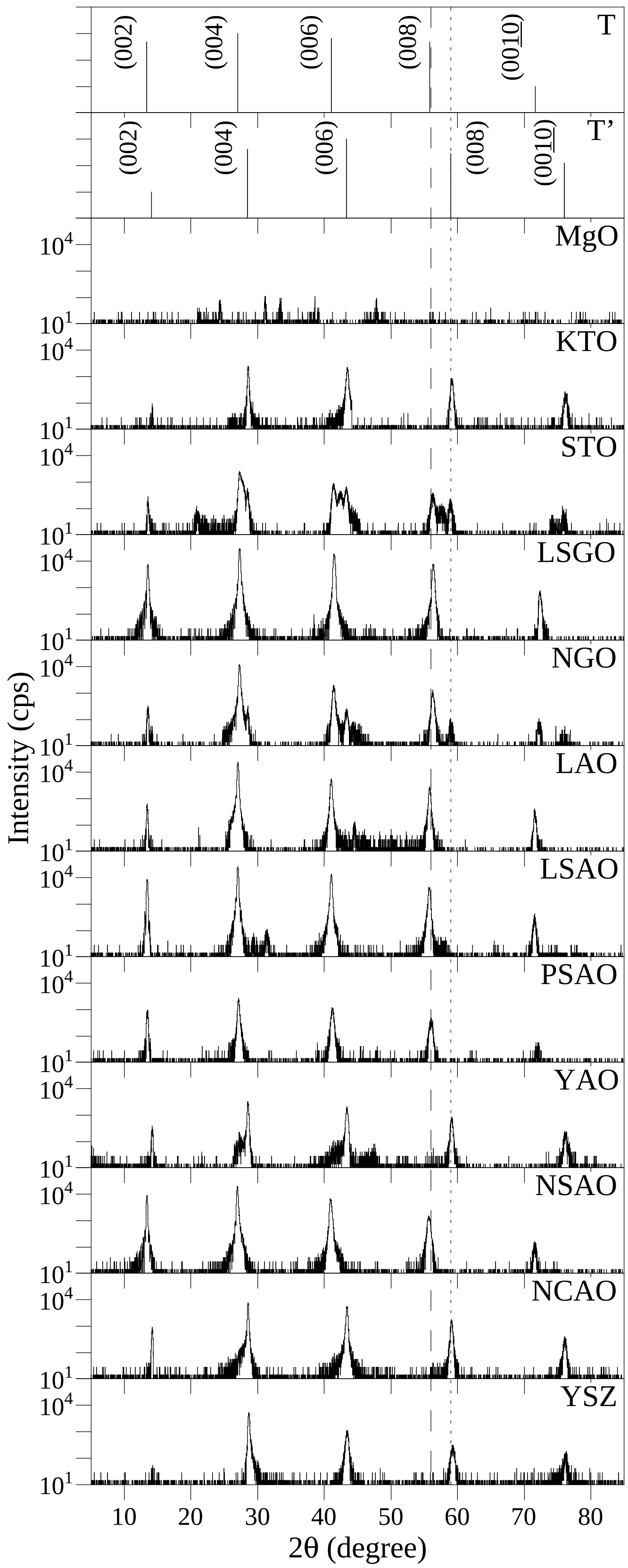

FIG. 2: XRD patterns for La_2CuO_4 films grown on various substrates at $T_s = 525°C$. The top two patterns are simulations for the T and T' structure. Substrate peaks are removed. The broken and dotted lines indicate the peak positions of the (008) line for the T and T' structure, respectively.

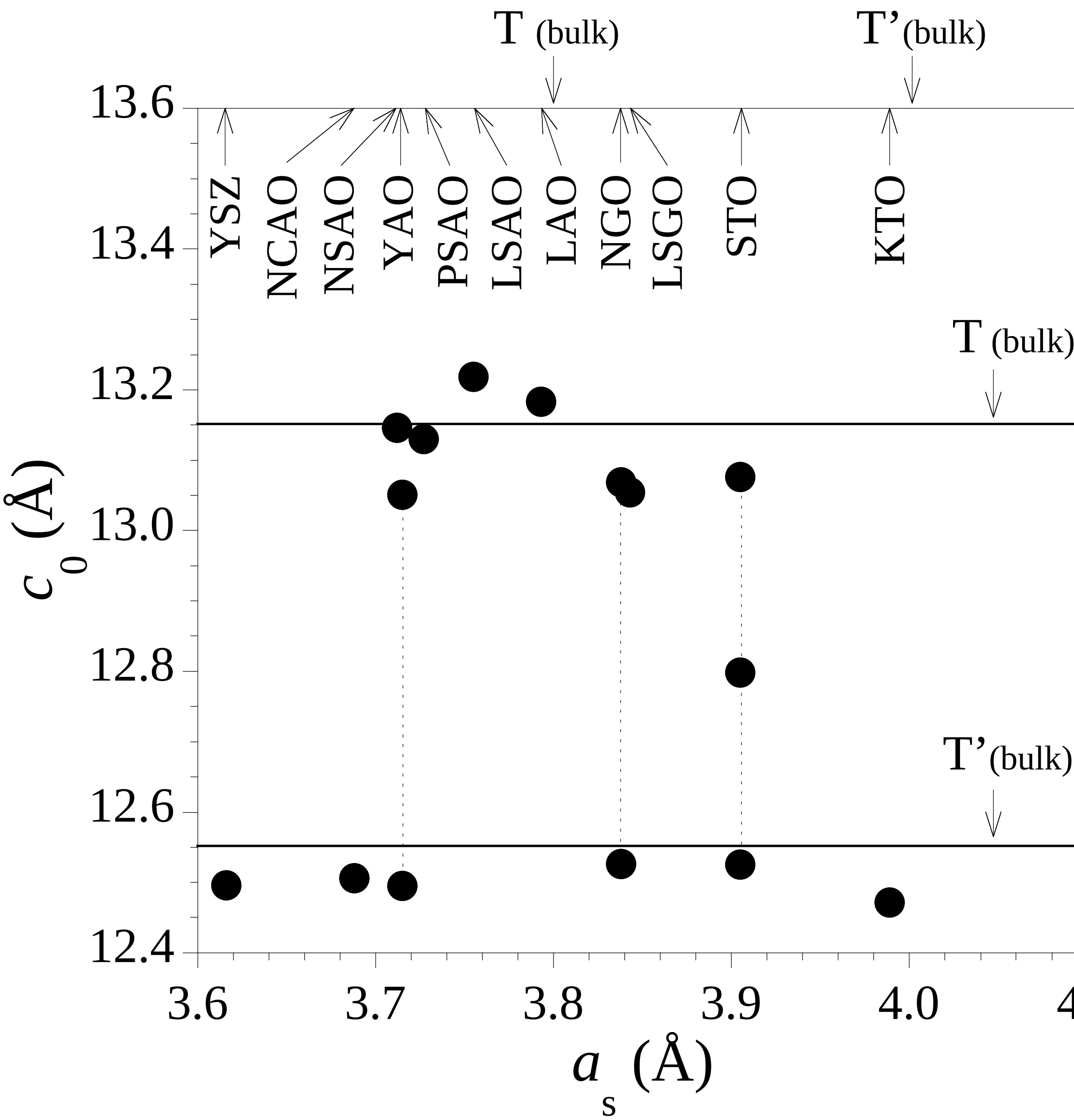

FIG. 3: Film's c_0 versus substrates a_s for La_2CuO_4 films grown at T_s = 525°C on different substrates. The lattice constants of bulk T- and T'-La_2CuO_4 (a_0 = 3.803 Å, c_0 = 13.15 Å for T and a_0 = 4.005 Å, c_0 =12.55 Å for T') are indicated by arrows together with a_s of the substrates. The circles connected by the vertical dotted lines indicate multi-phase formation. The c_0 values of the T structure is noticeably substrate-dependent because of epitaxial strain: the longest (c_0 = 13.25 Å) for LSAO and the shortest (c_0 = 13.05 Å) for LSGO. The c_0 value of 12.8 Å on STO seems to correspond to the T^*-like phase.

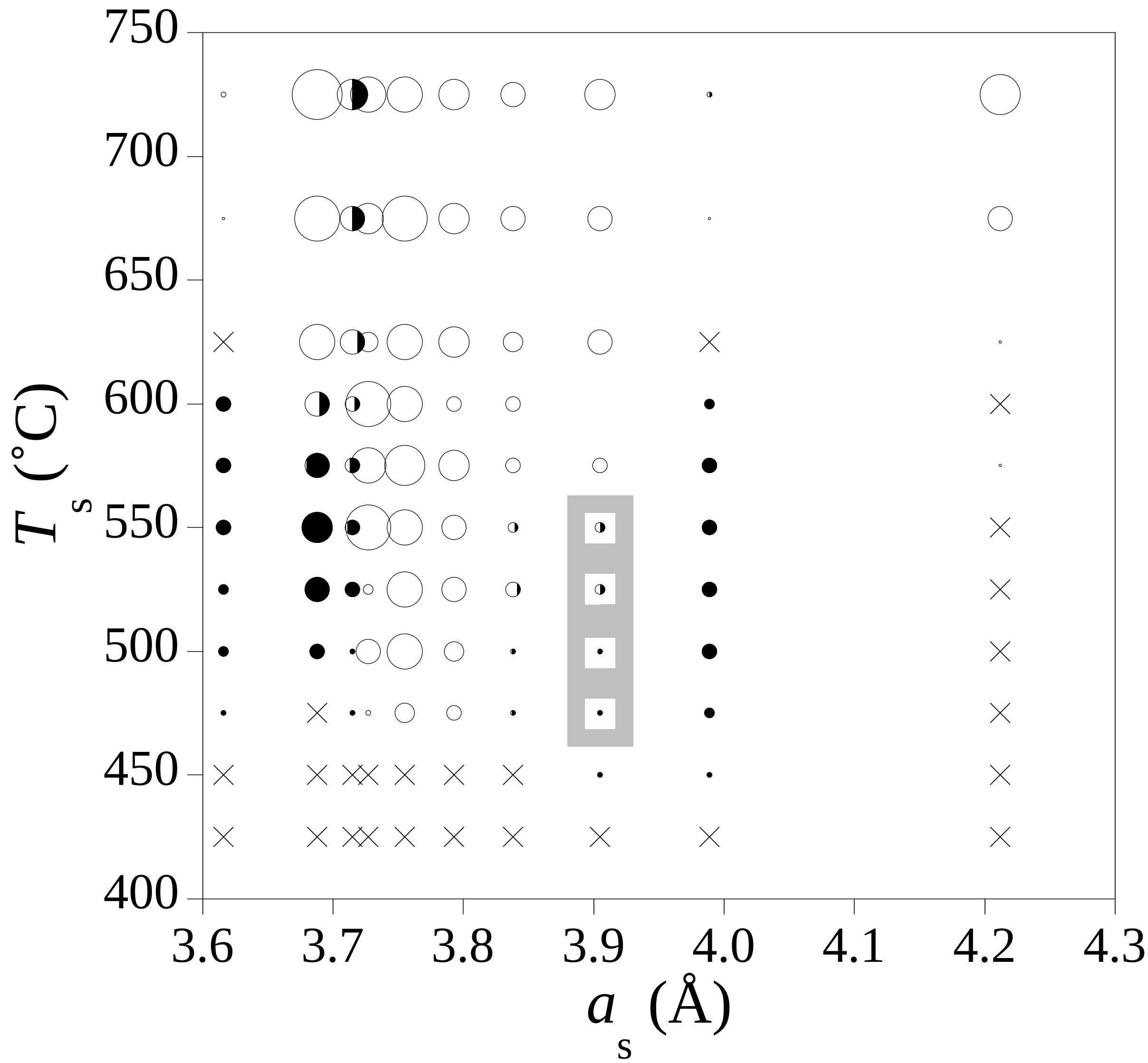

FIG. 4: Phase diagram on the selective stabilization of T versus T' in the T_{s} - a_{s} plane. The crosses indicate no phase formation. The open circles represent single-phase T while the filled circles represent single-phase T'. The partially filled circles represent a two-phase mixture. The size (area) of the circles is proportional to the XRD peak intensities of the (006) lines. For two-phase mixed films, the ratio of the unshaded and the shaded areas represent the ratio of the T and T' peak intensity of the (006) line. The results on LSGO and NSAO substrates are not included to avoid overlapping with the results on NGO and YAO. On LSGO and NSAO, the T structure is formed for $725^{\circ}\mathrm{C} > T_{\mathrm{s}} > 475^{\circ}\mathrm{C}$, and the T' structure is not formed for any T_{s}. The gray area at $a_{\mathrm{s}} = 3.905$ Å (STO) indicate the formation of the T*-like phase.

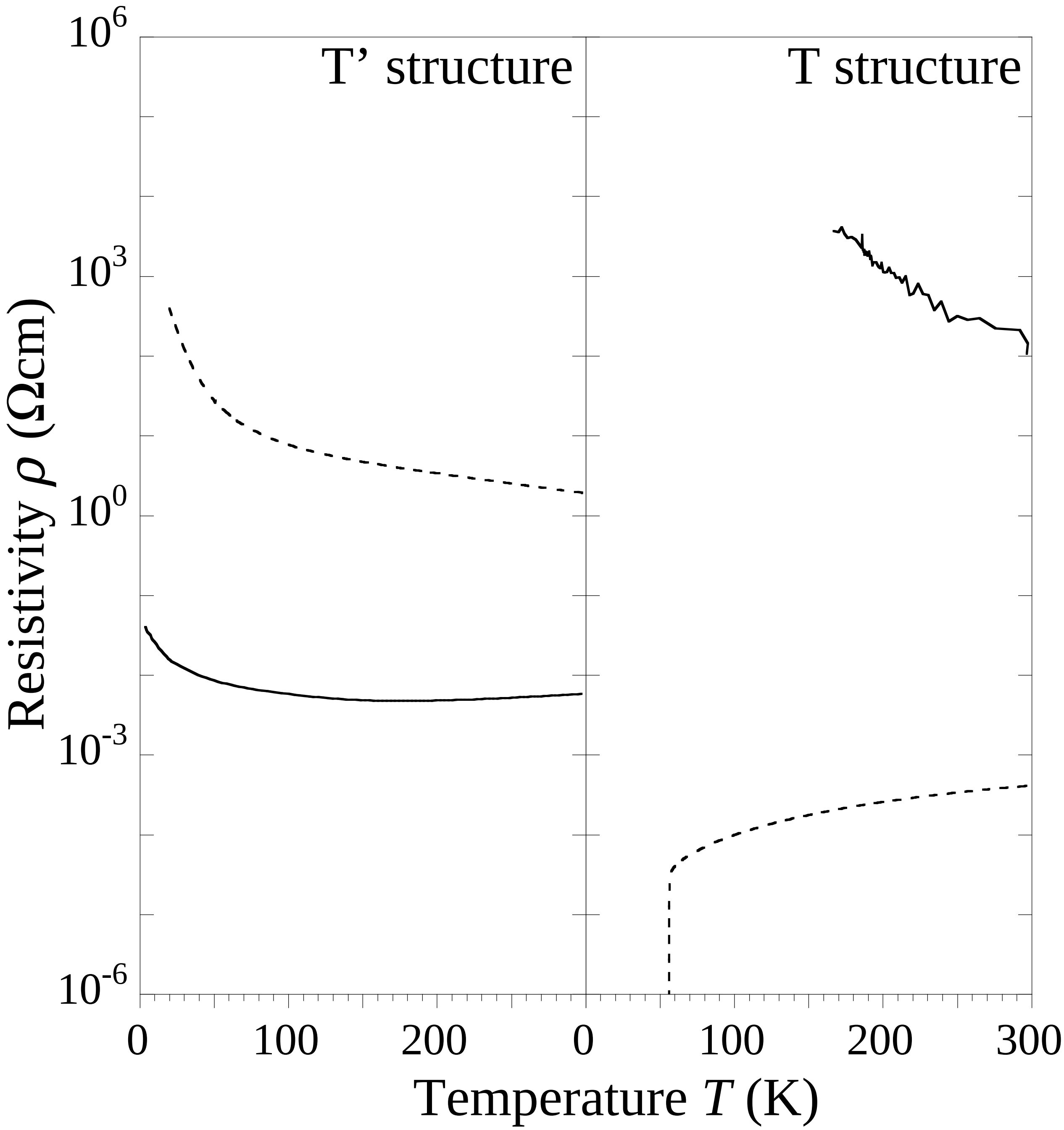

FIG. 5: Comparison of resistivity (ρ) - temperature (T) curves between T-$La_2CuO_{4+\delta}$ and T'-$La_2CuO_{4+\delta}$ films. The solid lines are for films cooled in vacuum ($\delta \sim 0$) while the broken lines are for films cooled in ozone ($\delta > 0$). With vacuum cooling, the T film has much higher resistivity than the T' film. Ozone cooling causes a totally opposite effect on T and T': the T film gets metallic and superconducting whereas the T' film gets more insulating.